Motomura's modified equation for surfactant penetration into spread monolayers

N.S. Santos Magalhães a,*, H.M. de Oliveira b, A. Baszkin c

a Laboratório de Imunopatologia Keizo-Asami, UFPE, Av. Moraes Rego, 1235 Cid. Universit., 50670-901 Recife-PE, Brazil
b Departamento de Eletrônica e Sistemas, UFPE, Rua Ac. Hélio Ramos s/n, Cid. Universit, 50738-420 Recife-PE, Brazil
c Physico-Chimie des Surfaces, URA CNRS 1218, Université Paris Sud, 5 rue J.B. Clément, 92296 Châtenay-Malabry, France

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Abstract

The extent of surfactant penetration into monolayers is often evaluated by thermodynamic approaches. The most formal treatment of the penetration phenomenon is due to Motomura et al. [K. Motomura, Y. Hayami, M. Aratono and R. Matuura, J. Colloid Interface Sci., 87 (1982) 333–338]. However, this model seems to be inadequate to determine adsorption into films in the condensed state. It is also in contradiction with Hall's [O.G. Hall, Langmuir, 2 (1986) 809] work which demonstrated that it is impossible to calculate penetration quantities without extra thermodynamic assumptions. We present here a modified equation for determination of thermodynamic quantities of penetration and calculate the adsorption of poly(oxyethylene)-poly(oxypropylene) block copolymers into soya phospholipid films using our previously obtained experimental data. The proposed modified Motomura equation may yield penetration quantities more reasonable than those obtained with the use of the Alexander–Barnes or classical Motomura equations. It also indicates why the known penetration models give such different adsorption values. Moreover, these contributions allow one to clarify the relationship between different approaches aimed at quantifying surfactant penetration into insoluble films.

Keywords: Equilibrium penetration; Hall's thermodynamic treatment; Mixed monolayer; Phospholipids; Poly(oxyethylene)-poly(oxypropylene) copolymer; Surfactant adsorption; Thermodynamic treatment of penetrations

1. Introduction

The extent of surfactant penetration into monolayers spread at the air/water interface has often been evaluated by different thermodynamic approaches. The most general and rigorous treatment of penetration phenomena is due to Motomura et al. [1]. The surface penetration phenomenon was also addressed by Ter-Minassian–Saraga [2] who derived (by another method) a similar equilibrium penetration equation. In contrast with other methods [3,4], Motomura's equation can be used to evaluate surfactant adsorption into films in the expanded state. However, such a model seems to be unsatisfactory to determine adsorption into films in the condensed state. Referring to the negative adsorption values found for penetration of hexadecyltrimethylammonium bromide into cholesterol monolayers, Alexander et al. [5] stated that "... while this result is
plausible in a quantitative sense, the depth from which surfactant would need to be excluded is unacceptably great" (sic). Similar results have also been observed by us for the penetration of soya phospholipid monolayers by poly(oxyethylene)-poly(oxypropylene) block copolymer injected into the underlying aqueous phase [6].

Hall's thermodynamic analysis [7] shows that it is impossible to solve the penetration problem (how to obtain \( \Gamma \) for the penetrating molecule from \( \pi-c-\Gamma_{film} \) data) without introducing non-thermodynamic assumptions. Since the approach of Motomura et al. does not require any extra hypothesis, there exists an incompatibility with Hall's result.

We shall focus here on the incompatibility of penetration quantities calculated from the Alexander–Barnes equations and the equation of Motomura et al. Although both approaches are intended to quantify surfactant adsorption, there is no clear relationship between them. We intend therefore to show that a certain modification of Motomura's equation is necessary in order to adapt it for films in the condensed state. We thus derive a new equation for adsorption calculations. The modified equation has been used to quantify the equilibrium penetration of poly(oxyethylene)-poly(oxypropylene) block copolymer into soya phospholipid monolayers from the data reported by Santos Magalhães et al. [6].

2. On surfactant adsorption into films

The Hansen thermodynamic approach [8,9] applied for a monolayer penetrated by a single surfactant gives the following equation describing the equilibrium surface tension \( \gamma_S \) of the systems:

\[
\frac{d\gamma_S}{\gamma} = -S^H dT + V^H dP - \Gamma_S^H d\mu_S - \Gamma_M^H d\mu_M
\]

(1)

where the superscript \( H \) refers to Hansen quantities, subscripts \( M \) and \( S \) stand for monolayer and surfactant respectively, \( \mu_i \) is the chemical potential of compound \( i \), and \( S^H \) and \( V^H \) are the excess entropy and the volume at the interface respectively. Assuming temperature \( T \) and pressure \( P \) to be constant and applying Alexander–Barnes notation [4] we obtain Eq. (1) in the form:

\[
d\pi_S = RT \Gamma_M^H d \ln \lambda_M + RT \Gamma_S^H d \ln \lambda_S
\]

(2)

Here, \( \lambda_i \) denotes the absolute activity of substance \( i \), \( \pi_S \) is the surface pressure of the mixed film and \( R = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1} \) is the gas constant.

Combining Eq. (2) with that derived by Motomura et al. [1] we obtain:

\[
d(\ln \lambda_M - \lambda_M - \pi_S/RT) = -\frac{1}{RT} \pi_S d\lambda_M - \lambda_M \Gamma_S^H d \ln \lambda_S
\]

(3)

where \( \lambda_M \) stands for the area per molecule of the film-forming substance.

Assuming that surfactant activities in the dilute solution are very low, we may consider that \( \lambda_S = m_S \), where \( m_S \) is the surfactant concentration. The application of the Maxwell relationship to the above equation promptly yields:

\[
\frac{1}{RT} \left( \frac{\partial \pi_S}{\partial \ln m_S} \right)_{T,P,\lambda_M} = \left( \frac{\partial \lambda_M \Gamma_S^H}{\partial \lambda_M} \right)_{T,P,m_S}.
\]

(4)

Independently, the surfactant adsorption on the monolayer-free interface can be calculated from the Gibbs equation according to the expression

\[
\frac{1}{RT} \left( \frac{\partial \pi_S^0}{\partial \ln m_S} \right)_{T,P,\lambda_M \rightarrow +\infty} = \Gamma_S^0
\]

(5)

where \( \Gamma_S^0 \) denotes the surfactant adsorption at the air/water interface, the superscript 0 standing for a monolayer-free system.

We then define the following variation quantities:

\[
\Delta \Pi_S \equiv \pi_S - \pi_S^0\quad (6a)
\]

and

\[
\Delta \Gamma_S \equiv \Gamma_S^H - \Gamma_S^0\quad (6b)
\]

Subtracting Eq. (4) from Eq. (5), we have

\[
\left( \frac{\partial \Delta \Pi_S}{\partial \ln m_S} \right)_{T,P,\lambda_M} = RT \left( \frac{\partial \lambda_M \Delta \Gamma_S}{\partial \lambda_M} \right)_{T,P,m_S}.
\]

(7)

This expression corresponds to that which is known as the Motomura equation [Eq. (9) in the paper of Motomura et al. [1]].

However, the integration of the above equation should be carried out more precisely than was
done by Motomura et al. Let us remark first that \( \Gamma_S^H \) tends to \( \Gamma_S^0 \) as \( \tilde{A}_M \) increases, so that

\[
\lim_{\tilde{A}_M \to +\infty} \Delta \Gamma_S = 0
\]

(8)

When the molar area \( \tilde{A}_M \) increases indefinitely the limit \( \tilde{A}_M \Delta \Gamma_S \) yields an indetermination \((0.\infty)\):

\[
\lim_{\tilde{A}_M \to +\infty} \tilde{A}_M \Delta \Gamma_S = K
\]

(9)

We shall see that the crux of the matter is the evaluation of \( K \) which eventually could be zero, finite or infinite. The unknown constant \( K \) is easily shown to be

\[
\lim_{r_m \to 0} \frac{\partial \Pi_s^H}{\partial \ln m_s} = \frac{1}{RT} \int_{\tilde{A}_M \Delta \Gamma_S}^{+\infty} \left( \frac{\partial \Pi_s}{\partial \ln m_s} \right)_{T,P,\tilde{A}_M} \cdot d \tilde{A}_M
\]

and, as indicated by Hall’s Eq. (8), the above limit is expected to remain finite. The integration of Eq. (7) (in the way proposed by Riemann-Stieljes [10]) within the interval from \( \tilde{A}_M \) to infinity yields:

\[
K = \int_{\tilde{A}_M \Delta \Gamma_S}^{+\infty} \left( \frac{\partial \Pi_s}{\partial \ln m_s} \right)_{T,P,\tilde{A}_M} \cdot d \tilde{A}_M
\]

(10)

so that

\[
-\tilde{A}_M \Delta \Gamma_S = \frac{1}{RT} \int_{\tilde{A}_M \Delta \Gamma_S}^{+\infty} \left( \frac{\partial \Pi_s}{\partial \ln m_s} \right)_{T,P,\tilde{A}_M} \cdot d \tilde{A}_M - K
\]

(11)

and finally

\[
\Gamma_S^H = \Gamma_S^0 - \frac{1}{\tilde{A}_M} \left[ \frac{1}{RT} \int_{\tilde{A}_M}^{+\infty} \left( \frac{\partial \Pi_s}{\partial \ln m_s} \right)_{T,P,\tilde{A}_M} \cdot d \tilde{A}_M - K \right]
\]

(12)

From Eq. (12) it is immediately apparent that the surfactant adsorption \( \Gamma_S^H \) approaches \( \Gamma_S^0 \) as \( \tilde{A}_M \) approaches infinity. Furthermore, it should be pointed out that under the assumption that \( K \) is zero Eq. (12) reduces to that proposed by Motomura et al. (i.e. Eq. (10) in Ref. [1]). However, the veracity of Eq. (12) has still to be verified using different experimental data. It should also be stressed that surfactant adsorption depends on the molar area of the film-forming substance, i.e. \( \Gamma_S^H = \Gamma_S^H(\tilde{A}_M) \).

It is worthwhile to mention that similar reasoning applies to Ter-Minassian-Saraga’s approach since the integration Eq. (AIV') = (AV') (Ref. (2), p. 394) involves a

\[
\lim_{a_1 \to +\infty} \Pi_s(\mu_2, a_1) \cdot a_1.
\]

According to Eq. (12) and despite \( K \neq 0 \), for films in the expanded state (high \( \tilde{A}_M \) values), the use of the Motomura equation leads to reasonable results for \( \Gamma_S^H \).

One now has to find a way to determine the term \( K \). For this purpose let us make an assumption based on the fact that adsorption is negligible near to the collapse of a monolayer. Therefore we put:

\[
\Gamma_S^H(\tilde{A}_M) \approx 0
\]

(13)

where \( \tilde{A}_M \) stands for the area per molecule of a film-forming amphiphilic compound at collapse. Substituting Eq. (12) into Eq. (13), we first find the approximation:

\[
\Gamma_S^H \approx \Gamma_S^0 \left[ 1 - \frac{\tilde{A}_M}{\tilde{A}_M} \right]
\]

(14)

It is worthwhile noting that the Alexander–Barnes equation was derived from that of Pethica [3,4] using the concept of the partial molar area. The Alexander–Barnes equation states:

\[
\Gamma_S = \frac{1}{RT} \left( 1 - \frac{\tilde{A}_M}{\tilde{A}_M} \right) \left( \frac{\partial \Pi_s}{\partial \ln m_s} \right)_{T,P,\tilde{A}_M}
\]

(15)

reducing to \( \Gamma_S = 0 \) when \( \tilde{A}_M = \tilde{A}_M \).

In terms of partial molar areas of constituents, the total area \( A \) at the interface is given by \( A = n_m \tilde{A}_M + n_s^H \tilde{A}_S \), where \( n_m \) is the number of spread film-forming molecules at the surface and \( n_s^H \) is the number of adsorbed surfactant molecules at the interface. It follows that \( \tilde{A}_M \tilde{A}_M + \tilde{A}_S \tilde{A}_S = 1 \), or

\[
\Gamma_S^H = \left[ 1 - \frac{\tilde{A}_M}{\tilde{A}_M} \right] \frac{1}{\tilde{A}_S}
\]

(16)

Eq. (16) implies that no surfactant adsorption
occurs at the molar area equal to the partial molar area at the surface. Therefore, it may be asserted that $I^\text{th} = 0$ for $A_M = \tilde{A}_M$, so that $I^\text{th} = (\tilde{A}_M) = 0$.

Under similar conditions, the proposed modified Motomura equation yields:

$$I^\text{th} = \left[ 1 - \frac{\tilde{A}_M}{\tilde{A}_M} \right] \frac{1}{RT} \frac{\partial}{\partial \ln m_S} m_S \bigg|_{T,P,\tilde{A}_M \to \infty}$$

$$+ \frac{1}{RT} \tilde{A}_M \frac{d}{d \ln m_S} m_S \bigg|_{T,P,\tilde{A}_M \to \infty} \cdot d \tilde{A}_M$$

(17)

The above equation resembles somewhat a modification of the Motomura equation proposed by Siegel and Vollhardt (Eq. (5) in Ref. [11]). However, in contrast to their equation, Eq. (17) naturally includes a “geometrical factor” and limiting cases such as $A_M \to \tilde{A}_M$ and $\tilde{A}_M \to +\infty$.

Since $I^\text{th} = 0$ is independent of $\tilde{A}_M$, Eq. (17) reduces to

$$I^\text{th} = \frac{1}{RT} \tilde{A}_M \frac{\partial}{\partial \ln m_S} m_S \bigg|_{T,P,\tilde{A}_M}$$

(18)

As the partial molar area $\tilde{A}_M$ of a mixed film is unknown, we use the mean value theorem [10] to solve the integral in Eq. (18). This gives:

$$I^\text{th} = \frac{1}{RT} \left[ 1 - \frac{\tilde{A}_M}{\tilde{A}_M} \right] \frac{\partial}{\partial \ln m_S} m_S \bigg|_{T,P,\tilde{A}_M}$$

(19)

Usually, $\tilde{A}_M < \tilde{A}_M$ so that $\tilde{A}_M < \tilde{A}_M < \tilde{A}_M < +\infty$. Hence, Eq. (19) is virtually the same as Eq. (15), especially for incompressible films for which $\tilde{A}_M \approx \tilde{A}_M$.

The area $\tilde{A}_M$ may be considered as the partial molar area of a surfactant in a mixed monolayer expressed in units of “equivalent area” of the film-forming substance:

$$\frac{1}{\tilde{A}_S} = \frac{1}{\tilde{A}_S} \frac{\partial}{\partial \ln m_S} m_S \bigg|_{T,P,\tilde{A}_M}$$

(20)

Eq. (19) can also be related to the “accessible area” theory describing the equilibrium penetration of a surfactant into a monolayer-covered surface [12,13]. According to this theory, the surfactant penetration quantity $I^\text{th}$ is given by

$$I^\text{th} = I^\text{th} - \alpha_M I^\text{th}(1/\tilde{A}_M)$$

(21)

where $I^\text{th}$ stands for adsorption into the accessible area, and $\alpha_M$ is the apparent cross-sectional area of a monolayer molecule. Comparison of Eqs. (19) and (21) gives:

$$I^\text{th} = \frac{1}{RT} \frac{\partial}{\partial \ln m_S} m_S \bigg|_{\tilde{A}_M}$$

$$\text{and} \quad \alpha_M = \tilde{A}_M$$

(22)

Moreover, as expected,

$$\lim_{\tilde{A}_M \to +\infty} I^\text{th} = I^\text{th}$$

Thus, the area $\tilde{A}_M$ may also be accounted for by the accessible area of the surface for adsorption. This alternative interpretation vindicates our arguments about surfactant adsorption evaluation.

3. Modified equation of the thermodynamic quantities of penetration

Combining Eqs. (16) and (17), it is possible to establish the relationship between partial molecular areas of film-forming constituents in a mixed monolayer:

$$\tilde{A}_S = \frac{RT}{\tilde{A}_M} \frac{\tilde{A}_M - \tilde{A}_M}{\tilde{A}_M}$$

(23)

The plot of $\tilde{A}_S$ vs. $\tilde{A}_M$ gives an “admissible partial areas curve”. Unfortunately, the modified Motomura approach presents the same drawback as other adsorption calculation equations, namely the fact that the molar area of the film-forming substance is unknown. Therefore, the surfactant adsorption quantity cannot be found from Eq. (23) and an additional equation is needed which is in perfect agreement with Hall’s work [7]. Usually, Pethica’s hypothesis has been used to circumvent this difficulty, but two conditions are required: firstly, the monolayer should be incompressible; and secondly, it holds true only for the monolayer in the condensed state. One of the possible ways to get out of this deadlock is to use the data from a “surface pressure vs. surface area” isotherm of a pure spread film, which is usually in a sigmoid form $\pi_M = S(\tilde{A}_M)$. We formulate then a “generalized Pethica hypothesis” as follows.
The surface pressure of a mixed film may be
related to the surface pressure of the monolayer-
free system and to that of a pure monolayer at the
partial molar area of the film by

$$\frac{n_{H}^{S}}{n_{H}^{S} + n_{M}^{S}} + \frac{n_{M}^{S}}{n_{H}^{S} + n_{M}^{S}} = S(\bar{A}_{M}) = \pi_{S}$$  \hspace{1cm} (24)$$

We promptly verify that under Pethica's assump-
tions the surfactant adsorption is low \((n_{H}^{S} \ll n_{M}^{S})\), so
that our hypothesis simplifies to what is known as
Pethica's hypothesis \([3]\).

Eq. (24) can be rewritten as

$$\Gamma_{S}^{H} \pi_{S} + \Gamma_{M} S(\bar{A}_{M}) = \pi_{S} (\Gamma_{S}^{H} + \Gamma_{M})$$  \hspace{1cm} (25)$$

which leads to the relationship

$$(\bar{A}_{M} - \bar{A}_{S}) \pi_{S} = \bar{A}_{S} S(\bar{A}_{M}) = \pi_{S} [(\bar{A}_{M} - \bar{A}_{S}) + \bar{A}_{S}]$$  \hspace{1cm} (26)$$

It is well known that the increase in the surfactant
adsorption brings about the increase in the surface
pressure of the film. Therefore, Eq. (24) appears to
be sufficient to account for the pressure increase.
In fact, as a result of the surfactant adsorption,
the molar fraction of the film-forming substance is
diminished \((\bar{A}_{M} < \bar{A}_{S})\). The surface pressure of the
mixed film, \(\pi_{M} \equiv S(\bar{A}_{M})\), may be higher than that
of a monolayer or surfactant alone. Hence a two-
component, two-ordinate, non-linear system is
obtained from Eqs. (23) and (26):

$$\begin{cases} (\bar{A}_{M} - \bar{A}_{S}) \pi_{S} + \bar{A}_{S} S(\bar{A}_{M}) = \pi_{S} [(\bar{A}_{M} - \bar{A}_{S}) + \bar{A}_{S}] \hspace{1cm} (27a) \\ \bar{A}_{S} = RT \frac{\bar{A}_{M} - \bar{A}_{S}}{\int_{\bar{A}_{M}}^{\bar{A}_{M}} \left( \frac{\partial \pi_{S}}{\partial \ln m_{S}^{S}} \right)_{T, P, A_{M}} d \bar{A}_{M}} \hspace{1cm} (27b) \end{cases}$$

Solving Eq. (27) for the partial molar area \(\bar{A}_{S}\)
of the surfactant, one can derive the adsorption \(\Gamma_{S}^{H}\) at the Hansen interface from Eq. (16).

The surfactant and the film-forming molecular
ratios at the interface can easily be computed from
the following two equations:

$$n_{H}^{S} \% = \frac{n_{H}^{S}}{n_{M}^{S} + n_{H}^{S}} = \frac{\Gamma_{S}^{H}}{\Gamma_{S}^{H} + \Gamma_{M}} = \frac{\bar{A}_{M} - \bar{A}_{S}}{\bar{A}_{M} + \bar{A}_{S}}$$  \hspace{1cm} (28)$$

and

$$n_{M} \% = \frac{n_{M}^{S}}{n_{M}^{S} + n_{H}^{S}} = \frac{\Gamma_{M}}{\Gamma_{S}^{H} + \Gamma_{M}} = \frac{\bar{A}_{S}}{\bar{A}_{M} - \bar{A}_{S} + \bar{A}_{S}}$$  \hspace{1cm} (29)$$

with \(n_{M} \% + n_{H} \% = 1\). With the known number of
spread film-forming molecules \(n_{M}\), the number of
surfactant molecules adsorbed into a monolayer
may be calculated provided that adsorption is not
negative.

The system described by Eqs. (27) can be solved
using a numerical method with a computer pro-
gram. More specifically, numerical computations of
\(\bar{A}_{S}\) can be done by increasing \(\bar{A}_{M}\) in small
increments from the collapse pressure so that both
Eqs. (27a) and (27b) yield identical solutions
(within a tolerance level). We have then:

3.1. Algorithm for finding partial areas in a mixed
monolayer

S1. Initial conditions: \(i = 0; \bar{A}_{M0} \equiv \bar{A}_{M}^{0}\).

S2. Updating: \(i = i + 1; \bar{A}_{M}^{i} \equiv \bar{A}_{M}^{i-1} + \Delta\).

S3. Partial area computations: \(\bar{A}_{S1}^{i}, \bar{A}_{S2}^{i}\)

$$\bar{A}_{S1}^{i} \equiv \frac{(\pi_{S} - \pi_{S}^{0}) [\bar{A}_{M} - \bar{A}_{M}^{i}]}{S(\bar{A}_{M}^{i}) - \pi_{S}}$$

$$\bar{A}_{S2}^{i} \equiv RT \frac{\bar{A}_{M} - \bar{A}_{M}^{i}}{\int_{\bar{A}_{M}^{i}}^{\bar{A}_{M}} \left( \frac{\partial \pi_{S}}{\partial \ln m_{S}^{S}} \right)_{T, P, A_{M}} d \bar{A}_{M}}$$

S4. If \(|\bar{A}_{S1}^{i} - \bar{A}_{S2}^{i}| < \epsilon\) then stop; otherwise go
to S2.

The solution of the algorithm yields the partial
areas \(\bar{A}_{M}\) and \(\bar{A}_{S}\) from which the surfactant
adsorption may be computed from:

$$\Gamma_{S}^{H} = \left[ \frac{\bar{A}_{M} - \bar{A}_{M}}{\bar{A}_{M}} \right] \frac{10^{20}}{N_{A} \bar{A}_{S}} \mu \text{mol} \text{ m}^{-2}$$  \hspace{1cm} (30)$$

where \(N_{A}\) is Avogadro's number.

The data from the linear stepwise isotherm
(s curve \(\pi_{S} \times \bar{A}_{M}\)) were fitted by the linear
interpolation and the numerical integration was car-
ried out by a generalized Simpson formula with 10
equal parts, with a step \(h = (\bar{A}_{M} - \bar{A}_{M})/10\). Also,
the values of \(\left( \frac{\partial \pi_{S}}{\partial \ln m_{S}^{S}} \right)_{A_{M} + \Delta h}, \ i = 0, 1, 2, \ldots, 10\),
were obtained from linear interpolation. The
algorithm was implemented on a 486 PC microcomputer using TURBO PASCAL language.

4. Application of the model to the adsorption of poly(oxyethylene)-poly(oxypropylene) block copolymer into soya phospholipid monolayers

In order to verify whether this new approach enables one to obtain more precise values we have recalculated the penetration data of poly(oxyethylene)-poly(oxypropylene) block copolymer into soya phospholipid monolayer at a molecular area of the pure spread film ranging from $\tilde{A}_M = 108 - 182 \, \text{Å}^2 \text{molecule}^{-1}$ with a surfactant concentration of $m_s = 5 \times 10^{-7} \text{mol l}^{-1}$ at $T = 298 \, \text{K}$. The molecular area of the copolymer at the monolayer-free surface is $40.77 \, \text{Å}^2 \text{molecule}^{-1}$ [14]. A comparison of the penetration data obtained with the modified Motomura equation and those proposed by Alexander-Barnes gives the results summarized in Tables 1 and 2.

The admissible curve from our data furnishes a relatively robust estimate for $\tilde{A}_S$, i.e. the partial molar area of the surfactant remains almost unchanged over a wide range of partial molar area values of the film-forming substance. Fig. 1 illustrates such a behavior and shows graphically the solution of the non-linear two-equation system Eq. (27) in a particular interfacial system for which $\tilde{A}_M = 108 \, \text{Å}^2 \text{molecule}^{-1}$ and $m_s = 5 \times 10^{-7} \text{mol l}^{-1}$.

The surfactant is adsorbed into "gaps" in the monolayer. We consider the cross-sectional area $\tilde{A}_S$ of surfactant molecules adsorbed at the inter-

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**Table 1**

Partial molecular areas for block copolymer/phospholipid mixed film ($\gamma^* = 9.65 \, \text{mN m}^{-1}$ and $m_s = 5 \times 10^{-7} \text{mol l}^{-1}$)

<table>
<thead>
<tr>
<th>Pure phospholipid spread monolayer $\tilde{A}_M$</th>
<th>Alexander-Barnes</th>
<th>Modified Motomura</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tilde{A}_M$</td>
<td>$\tilde{A}_S$</td>
</tr>
<tr>
<td>102</td>
<td>95.7</td>
<td>353.0</td>
</tr>
<tr>
<td>108</td>
<td>102.3</td>
<td>244.0</td>
</tr>
<tr>
<td>122</td>
<td>110.1</td>
<td>218.0</td>
</tr>
<tr>
<td>146</td>
<td>112.8</td>
<td>136.0</td>
</tr>
<tr>
<td>182</td>
<td>100.0</td>
<td>271.0</td>
</tr>
</tbody>
</table>

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**Table 2**

Copolymer adsorption into the phospholipid film (μmol m⁻²)

<table>
<thead>
<tr>
<th>Pure phospholipid spread monolayer $\tilde{A}_M$ (Å² molecule⁻¹)</th>
<th>Alexander-Barnes</th>
<th>Motomura</th>
<th>Modified Motomura</th>
</tr>
</thead>
<tbody>
<tr>
<td>102</td>
<td>0.030</td>
<td>-1.33</td>
<td>0.49</td>
</tr>
<tr>
<td>108</td>
<td>0.036</td>
<td>-0.83</td>
<td>0.011</td>
</tr>
<tr>
<td>122</td>
<td>0.074</td>
<td>0.14</td>
<td>0.060</td>
</tr>
<tr>
<td>146</td>
<td>0.28</td>
<td>1.31</td>
<td>0.16</td>
</tr>
<tr>
<td>182</td>
<td>0.28</td>
<td>2.49</td>
<td>0.68</td>
</tr>
</tbody>
</table>

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Fig. 1. Bidimensional partial area plot in a mixed phospholipid monolayer with one species adsorbed. $\tilde{A}_M = 108 \, \text{Å}^2 \text{molecule}^{-1}$ and $m_s = 5 \times 10^{-7} \text{mol l}^{-1}$. Admissible curve (●) for surfactant partial molecular area is shown.
face. At very high film coverage, the pure spread monolayer presents quite small holes so that surfactant may be adsorbed with just one molecule per hole. As a consequence, the partial molecular area of the surfactant tends to the area of the surfactant polar head, $40 \text{Å}^2 \text{molecule}^{-1}$. At low monolayer coverage, a large amount of surfactant per hole is adsorbed into the spread film and the partial molecular area of the surfactant also tends to the same value.

Fig. 2 shows the partial area of the monolayer-forming substance versus the molecular area of the pure spread film. The plot considers a surfactant concentration in the underlying phase of $m_s = 5 \times 10^{-7} \text{ mol l}^{-1}$. The values of $A_M$ are very close to those obtained by the Alexander–Barnes equation, especially for mixed films far from their condensed or expanded states. In the later case, we expect more plausible results using our approach. Copolymer adsorption into phospholipids is presently being evaluated over a wide range of surfactant concentrations.

Comparison of the equilibrium penetration values of phospholipid monolayer by a copolymer estimated according to three models are shown in Fig. 3. The modified Motomura equation furnishes somewhat similar surface excess concentrations $\Gamma_s$ to those from Alexander–Barnes. However, at low monolayer coverage and high surfactant concentration, adsorption values are halfway between Alexander–Barnes and Motomura levels. The penetration values obtained seem to be more reasonable than the Alexander–Barnes results since the surfactant adsorption at Hansen’s interface tends to 4.07 $\mu$mol m$^{-2}$ for films in the expanded state [6]. Moreover, the composition of the surface — $n_s = 0.75\%$ for an area per molecule of $A_M = 108 \text{ Å}^2 \text{molecule}^{-1}$ (near the condensed state), $n_s = 12.3\%$ for $A_M = 1.46 \text{ Å}^2 \text{molecule}^{-1}$, and $n_s = 42.9\%$ for $A_M = 182 \text{ Å}^2 \text{molecule}^{-1}$ (near the expanded state) — also seems to be realistic.

5. Conclusion

Penetration phenomena are not fully modeled or understood [5,11,15]. This work intended to present a new contribution to enable the evaluation

![Graph](https://via.placeholder.com/150)

**Fig. 2.** Partial molecular area of the film-forming substance for different monolayer coverages: (□) Alexander–Barnes; (●) modified Motomura.
of penetration into mixed films containing insoluble monolayers and one adsorbed species. Specifically, we have discussed the application of the approach of Motomura et al. to evaluate surfactant penetration into monolayers. Such an approach is often preferred because it is derived without extra-thermodynamic assumptions. However, in all data from the literature, the adsorption values calculated by this method differ appreciably from those calculated by the other procedures. Furthermore, they do not agree with Hall's conclusion which shows that such a problem is isomorphic with obtaining changes in the Galvani potential drops across a mercury/electrolyte solution interface as the solvent composition is varied [7]. A discrimination between these theories has long been sought. As a main contribution, our results reveal deficiencies in the classical model of Motomura et al. and suggest some refinements. New equations for adsorption phenomena have been derived which could explain the unrealistic (negative) results obtained by Motomura's equation for the films in their condensed state. They also elucidate the contradiction between the theories of Motomura and Hall. The evaluation of the surfactant adsorption obtained with these new equations makes possible narrowing of the gap between adsorption values calculated with the Alexander-Barnes equation and with that of Motomura. They may also indicate why the models give different values for the composition of surfaces [5,6,11]. Another interesting point to be mentioned is a potential relationship between the Pethica and Motomura equations and even with the accessible area theory. Additionally, the new approach allows one to find out the partial molecular area of the surfactant in the mixed monolayer. Finally, we suggest the application of the reviewed model to other interfacial systems in order to provide a better understanding of its validity, possible deficiencies and/or limitations.

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Appendix A\(^1\) (suggested by one of the reviewers): a Hansen interface model for surfactant equilibrium penetration of an insoluble monolayer at the air/water interface

We have presumed throughout this paper that \( I_{\beta}^{l} = n_{\beta}^{l} / A \). In order to assess the composition of the surface we require a hypothesis for the character of the Hansen interface, leading to a model of the interface. Here \( \alpha \) and \( \beta \) stand respectively for the gas phase (air) and the liquid phase (water). In the following calculations we assume that \( T = 298.15 \) K and \( P = 760 \) Torr and components \( i \) are \( w \) (water), \( N \) (nitrogen: for simplicity we neglect oxygen, argon, etc), \( M \) (monolayer) and \( S \) (surfactant).

The diagram illustrates a Hansen interface assuming a uniform composition both above the distance \( l_1 \) and below the distance \( l_2 \), which are taken to be about 100 nm, corresponding to \( 1 \times 10^{-4} \) m\(^2\). As usual, we assume that \( C_M \) is negligible in both liquid and gas phases \( (C_M^{l} = C_M^{g} = 0) \) and that \( C_S \) is negligible in the gas phase \( (C_S^{g} = 0) \). We take the partial molar volume of the surfactant in the liquid phase to be \( 8.35 \) l mole\(^{-1}\).

![Diagram of Hansen interface model](image_url)

Considering a surfactant concentration \( C_S \) varying from 0 to \( 5 \times 10^{-4} \), the density and vapor pressure of water and the solubility of nitrogen in water are available from Ref. [16] yielding:

Water: \( C_w^{l} = 1.279 \times 10^{-3} \) and \( C_w^{g} = 55.2 \)

Nitrogen: \( C_N^{l} = 3.959 \times 10^{-2} \) and \( C_N^{g} = 6.33 \times 10^{-4} \)

Note: rigorously, for \( 0 \leq C_S \leq 5 \times 10^{-4} \), one has \( C_S^{g} \) varying from 55.11 to 55.34 or 55.2 to a sufficient approximation. The equilibrium vapor pressure of water at 298.15 K is 23.77 Torr, unless the system is enclosed or the ambient humidity is 100% when there may be extensive water loss by evaporation — but we assume that this is not a problem.

We can ignore the regions above \( l_1 \) and below \( l_2 \) and consider just the subsystem between these regions (Ref. [8], p. 411):

\[
I_{\alpha}^{l} = n_1 - \lambda_\alpha C_1^{\alpha} - \lambda_\beta C_1^{\beta}
\]

Two degrees of freedom exist so we can define the interface setting \( I_{M}^{l} = I_{N}^{l} = 0 \) by choice of \( \lambda_\alpha \) and \( \lambda_\beta \). Therefore:

\[
\left( \begin{array}{c}
  n_M \\
  n_w \\
\end{array} \right) = \left( \begin{array}{cc}
  C_N^{l} & C_N^{g} \\
  C_w^{l} & C_w^{g} \\
\end{array} \right) \left( \begin{array}{c}
  \lambda_\alpha \\
  \lambda_\beta \\
\end{array} \right)
\]

The expression for \( \lambda_\beta \) and (and \( \lambda_\alpha \)) can then be recast:

\[
\lambda_\beta = \frac{n_w C_N^{l} - n_M C_w^{l}}{C_w^{g} - C_N^{g}}
\]

Remembering the concentrations we neglected, we can write \( I_{M}^{l} = n_M \) and \( I_{N}^{l} = n_S + \lambda_\beta C_S^{g} \). At this point it is convenient to assume that \( n_i = n_1^{l} + n_1^{g} + n_M^{l} \), corresponding to amounts in the \( l_1 \), \( l_2 \) and monolayer regions. To proceed further we need to assume a system model which is rather illustrative but still fairly reasonable. We assume that concentrations retain their distinct values right to the monolayer, i.e. \( n_1^{l} = l_1 C_1^{l} \) and \( n_1^{g} = l_2 C_1^{g} \). In the examined case (air/water)

\[
\frac{C_N^{l} \cdot C_w^{l}}{C_N^{g} \cdot C_w^{g}} < 1 (\approx 3.71 \times 10^{-7})
\]

---

\(^1\) The inclusion of this Appendix was suggested by one of the reviewers.
so, after a bit of routine algebra, we obtain:

\[ \Gamma_S^N \approx n_S^N - \frac{C_s}{C_w} n_w^N + \frac{C_N}{C_s} n_N^M \cdot n_N^N \]

Therefore the excess surfactant concentration at Hansen’s interface for a given surface area can be roughly given by \( \Gamma_S^N \approx n_S^M/A \), with negligible error for any reasonable values of \( n_w^M \) and \( n_N^N \).

**Appendix B: List of symbols**

- \( A \): total area at the interface
- \( \bar{A}_M \): area per molecule of the film-forming substance
- \( \bar{A}_M \): partial molar area of the film-forming substance
- \( \bar{A}_S \): partial molar area of the surfactant
- \( \bar{A}_S \): area per molecule of the film-forming amphiphilic compound at collapse
- \( \bar{A}_M \): Pethica’s partial molar area of a monolayer
- \( \bar{A}_M \): partial molar area of surfactant expressed in units of “equivalent area” of the film-forming substance
- \( \bar{a}_M \): apparent cross-sectional area of a monolayer molecule
- \( \bar{A}_S^{1/2} \): 1st surfactant partial molar area estimation according to generalized Pethica hypothesis
- \( \bar{A}_S^{1/2} \): 2nd surfactant partial molar area estimation according to the admissible curve
- \( n_s \): surfactant concentration (molality of surfactant)
- \( n_s^N \): number of adsorbed surfactant molecules at the interface
- \( n_{\bar{A}} \): number of spread film-forming molecules at the surface
- \( N_A \): Avogadro’s number
- \( P \): pressure
- \( R \): gas constant
- \( S^N \): excess entropy at the surface per unit area
- \( T \): temperature
- \( V^N \): excess volume at the surface per unit area

**Greek letters**

- \( \Delta \): partial area increment in the numeric solution (step)
- \( \Delta \): penetration variation quantity regarding the monolayer-free system
- \( \Delta \): surface pressure variation quantity regarding the monolayer-free system
- \( \epsilon \): stop criterion for the numerical algorithm
- \( \gamma_s \): equilibrium surface tension of the mixed monolayer
- \( \Gamma_S^N \): surface excess number of moles of penetrating substance at the interface
- \( \Gamma_M \): surface excess number of moles of film-forming substance
- \( \Gamma_s \): surfactant adsorption at the air/water monolayer-free system
- \( \Gamma_s \): surfactant penetration quantity
- \( \Gamma_w \): adsorption into the accessible area
- \( \lambda_i \): absolute activity of the substance \( i, i = S, M \)
- \( \mu_i \): chemical potential of species \( i, i = S, M \)
- \( \pi_s \): film surface pressure of the mixed film
- \( \pi_s^0 \): surface pressure of the monolayer-free system

**Subscripts**

- \( M \): monolayer molecules
- \( S \): surfactant molecules
- \( i \): compound \( i \) of the mixed film

**Superscripts**

- \( 0 \): monolayer-free system
- \( H \): Hansen quantities at the interface
- \( (i) \): \( i \)th numerical iteration

**References**


